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## EXPERIMENTS ON HEAVY ELECTRON AND HIGH $T_c$ OXIDE

### SUPERCONDUCTORS

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### INTRODUCTION

Two classes of superconducting materials, heavy electron superconductors (frequently referred to as "heavy fermion superconductors")<sup>1,2</sup> and superconducting oxides,<sup>3</sup> have attracted a considerable amount of attention in recent years because of their extraordinary superconducting properties which may be associated with an unconventional type of superconductivity. During the past year, two types of oxides containing a rare earth element (or yttrium), an alkaline earth element, and copper, have been found to exhibit superconductivity at high temperatures, one type at temperatures as high as  $\sim 100$  K! These spectacular developments have brought an unprecedented level of excitement and intensity to research on these new oxides and related materials.

The heavy electron materials, compounds of a rare earth element (usually Ce) or an actinide element (usually U), appear to have an enormous density of states  $N(E_F)$  at the Fermi level  $E_F$ , as inferred from  $\gamma$ , the coefficient of the electronic specific heat  $C_e = \gamma(T)T$ , which attains values as large as several J/mole-K<sup>2</sup> for some materials at temperatures  $T < 1$  K. Alternatively, the electrons can be viewed as having an immense effective mass as large as several hundred times the mass of the free electron. Since the specific heat jump  $\Delta C$  at the superconducting transition temperature  $T_c$  is of the order of  $\gamma(T_c)T_c$ , the same heavy electrons that are responsible for the large  $\gamma$  in the normal state are also involved in the superconductivity. The heavy electron superconductors have low  $T_c$ 's ( $\leq 1$  K) and, for such low  $T_c$ 's, extremely large upper critical magnetic fields  $H_{c2}$

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with anomalous temperature dependences. Superconducting properties such as the specific heat, thermal conductivity, magnetic field penetration depth, ultrasonic attenuation rate, and nuclear spin lattice relaxation rate have power law temperature dependences  $\sim T^n$ , where  $n$  is an integer, suggesting that these materials may exhibit anisotropic superconductivity in which the superconducting energy gap vanishes at points or lines on the Fermi surface.<sup>1</sup> An especially intriguing possibility is that the anisotropic superconductivity involves triplet-spin pairing of electrons,<sup>2</sup> mediated by paramagnon exchange, in analogy with superfluid  $^3\text{He}$ .

Compared to the heavy electron superconductors, the oxide superconductors have very low values of  $N(E_F)$ , as inferred from low values of the electronic specific heat coefficient  $\gamma$ . As a result, the specific heat jump  $\Delta C$  at  $T_c$  is very small and barely discernable in some of these materials [e.g., the compound<sup>3</sup>  $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ ]. In the '70's, superconductivity at moderately high temperatures was reported in two oxide systems,  $\text{Li}_{1-x}\text{Ti}_{2+x}\text{O}_4$  with  $T_c \sim 14$  K [Ref. 4] and  $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$  with  $T_c \sim 13$  K [Ref. 5]. Recently, superconductivity at high temperatures has been observed in two copper oxide compounds,  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-\delta}$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) which has a maximum  $T_c \approx 40$  K for  $M = \text{Sr}$  and  $x \approx 0.15$  [Refs. 6-9], and  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  which has a  $T_c \approx 90$  K for  $R = \text{Y}$  or a rare earth element (except for  $\text{Ce}, \text{Pr}$  or  $\text{Tb}$ ) [Refs. 10-14]. The unexpectedly large values of  $T_c$  displayed by these materials, especially in view of such low values of  $N(E_F)$ , has led to the speculation that these materials may display an unconventional type of superconductivity, perhaps similar in nature to that of the heavy electron compounds.

The feature that is common to the heavy electron superconductors and the high  $T_c$  superconducting oxides may be a magnetic mechanism that is responsible for the formation of the superconducting electron pairs (Cooper pairs). Such a magnetic pairing mechanism is, for example, incorporated in the "resonating valence bond" (RVB) model that was recently advanced by Anderson<sup>15</sup> to account for the high  $T_c$  superconductivity of the new copper oxide materials. In the RVB model, the superconducting electron pairs are identified with nearest neighbor pairs of  $\text{Cu}^{2+} S = 1/2$  electrons in spin-singlet states, as a result of the superexchange interaction, which become mobile when a sufficient number of  $\text{Cu}^{3+}$  ions are present. Lines of zeroes of the superconducting energy gap on the Fermi surface are also suggested which, along with the antiferromagnetic correlations involving the nearest-neighbor spin-singlets, may indicate a relationship between the RVB and heavy electron superconducting states.

In the first part of this paper, we briefly describe some of our efforts to determine the type of pairing and pairing mechanisms that are associated with the superconductivity of heavy electron materials by means of  $H_{c2}(T)$  measurements in Gd-doped  $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$  alloys. An account of some of our recent work on the new high  $T_c$  copper oxide superconductors is given in the second part of the paper.

#### UPPER CRITICAL MAGNETIC FIELD MEASUREMENTS ON Gd-DOPED $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$ ALLOYS

A striking  $T_c$  vs  $x$  phase diagram has been reported<sup>1, 16</sup> for the heavy electron system  $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$ ;  $T_c$  exhibits a nearly linear

decrease with  $x$ , a sharp minimum at  $x_{\min} \approx 0.017$ , a broad maximum at  $x_{\max} \approx 0.025$ , and a subsequent decrease with  $x$ . For compositions  $x$  between  $\sim 0.017$  and  $\sim 0.04$ , two features have been observed in the specific heat, the upper one associated with the development of the superconducting state and the lower one corresponding to another phase transition that occurs without destroying the superconductivity.<sup>17</sup> Two possible explanations for the lower peak are that (1) it is associated with a second superconducting phase with a different order parameter (in analogy with superfluid  $^3\text{He}$ ), and (2) that it is due to the formation of an itinerant electron antiferromagnetic state that coexists with superconductivity.

We have made measurements of  $T_c$  as a function of pressure  $P$  on the  $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$  system for  $0 \leq P \leq 12$  kbar.<sup>18</sup> The results indicate that there are two distinct superconducting phases in the  $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$  system, one in the region  $0 \leq x < x_{\min}$  (which we refer to as the A phase) and the other at  $x > x_{\min}$  (B phase), where  $x_{\min}$  is a function of  $P$ . Unfortunately, the  $T_c(P)$  measurements yielded no information about the nature of the phase transition in the superconducting state that is responsible for the lower peak in the specific heat for  $x > x_{\min}$ .

In order to probe the nature of the A and B superconducting phases in pure and Th-doped  $\text{UBe}_{13}$ , we have carried out  $H_{c2}(T)$  measurements on  $(\text{U}_{1-x}\text{Gd}_x)\text{Be}_{13}$  and  $[(\text{U}_{0.971}\text{Th}_{0.029})_{1-x}\text{Gd}_x]\text{Be}_{13}$  alloys for various values of  $x$ , the results of which are shown in Figs. 1(a) and (b), respectively.<sup>19</sup> The purpose of this experiment was to determine whether the A and B superconducting phases respond differently to  $\text{Gd}^{3+}$  ions whose  $S = 7/2$  spins would be expected to interact with the spins of the superconducting electrons via the exchange interaction. The data in Fig. 1(a) reveal that the Gd impurities have a strong effect on the  $H_{c2}(T)$  curves for pure  $\text{UBe}_{13}$  (A phase) which becomes more pronounced with increasing concentration of Gd. Specifically, the  $H_{c2}(T)$  curves develop an unusual "foot" in low fields and are generally depressed in magnitude and slope in higher fields. In contrast, the data in Fig. 1(b) show that the Gd impurities have virtually no effect on the shape of the  $H_{c2}(T)$  curves for  $(\text{U}_{0.971}\text{Th}_{0.029})\text{Be}_{13}$  (B phase).

The  $H_{c2}(T)$  curves of Gd-doped  $\text{UBe}_{13}$  reveal that the Gd spins have a strong destructive effect on the superconductivity of pure  $\text{UBe}_{13}$ . In fact, the shapes of the  $H_{c2}(T)$  curves of the Gd-doped  $\text{UBe}_{13}$  samples can be qualitatively described by the multiple pair breaking theory for a conventional type II superconductor<sup>20, 21</sup> if the primary mechanism for "breaking" superconducting electron pairs is the Zeeman interaction of the exchange field  $H_J$  associated with the Gd spins with the superconducting electron spins. This is illustrated in Fig. 2(a) where the calculated  $H_{c2}(T)$  curves for  $H_J = 0$  (solid lines) and  $H_J \neq 0$  (dashed lines) are compared to the data. The calculations of the  $H_{c2}(T)$  curves, which will be described elsewhere in detail, were based on the following parameters: spin-orbit scattering parameter  $\lambda_{so} = 2\hbar/3\pi\tau_{so}k_B T_{co} = 10$ , where  $\tau_{so}$  is the spin-orbit scattering lifetime; exchange interaction parameter  $J = 0.018$  eV [i.e.,  $H_J(H, T) = xJ(g_J - 1) < J > / 2 \mu_B$ , where  $x$  is the concentration of paramagnetic ions,  $g_J$  and  $J$  are, respectively, the Landé  $g$ -factor and total angular momentum of the rare earth ion's Hund's rule ground state], and a temperature dependence of the orbital critical field  $H_{c2}^o(T)$  that was chosen so that the pair breaking theory describes the  $H_{c2}(T)$  curve of pure

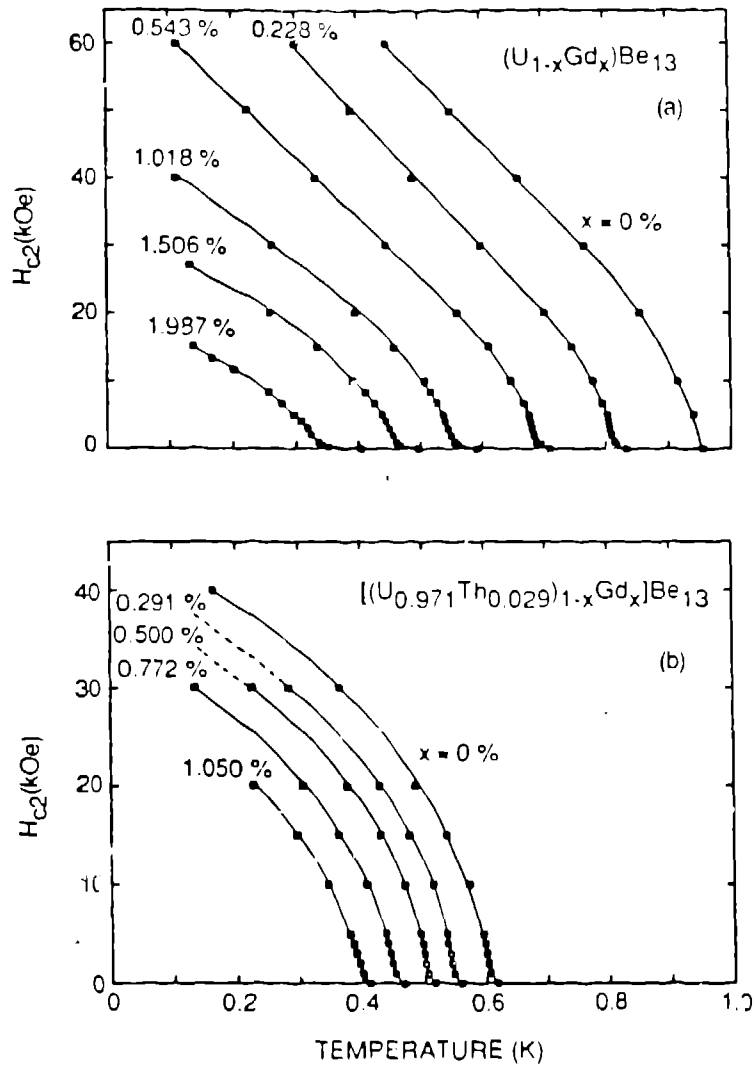


Fig. 1. Upper critical field  $H_{c2}$  vs temperature for (a)  $(U_{1-x}Gd_x)Be_{13}$  and (b)  $[(U_{0.971}Th_{0.029})_{1-x}Gd_x]Be_{13}$ . The lines are guides to the eye.

$UBe_{13}$ . The "foot" in the  $H_{c2}(T)$  curves could then result from the saturation of the Gd spins and, in turn, the exchange field and its "pair breaking" effect, in low fields and at low temperatures. However, the calculated  $H_{c2}(T)$  curves in Fig. 2(a) do not describe the low field data very well, although the discrepancy can be reduced by including a molecular field constant  $\theta$  as illustrated for the  $x = 1.987\%$  data. Nonetheless, within the limitations imposed by the simplifying assumptions that have been made, the multiple pair breaking theory with  $H_J \neq 0$  seems to provide a satisfactory qualitative description of the  $H_{c2}(T)$  data for Gd-doped  $UBe_{13}$ . Thus, the simplest interpretation of the  $H_{c2}(T)$  measurements would seem to favor singlet-spin pairing, perhaps of d-wave character, or BW (Balian-Werthamer) type triplet-spin pairing of superconducting electrons in  $UBe_{13}$ .

The  $H_{c2}(T)$  curves of Gd-doped  $(U_{0.971}Th_{0.029})Be_{13}$  indicate that the Gd spins have a negligible effect on the superconductivity of  $(U_{0.971}Th_{0.029})Be_{13}$ . This is depicted in Fig. 2(b) where the data are best described by the calculated  $H_{c2}(T)$  curves for  $H_J = 0$ . The insensitivity of the superconductivity of  $(U_{0.971}Th_{0.029})Be_{13}$  to the Gd exchange field suggests that this material may exhibit a qualitatively different type

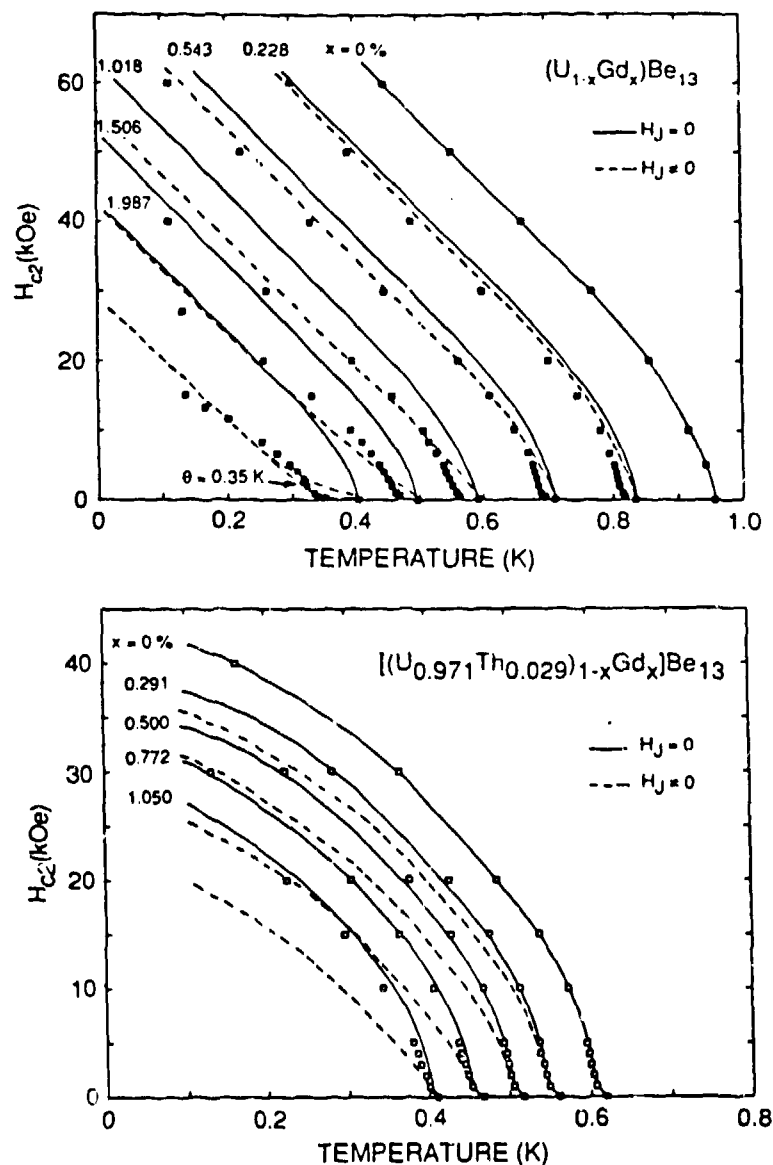


Fig. 2. Upper critical field  $H_{c2}$  vs temperature for  $(U_{1-x}Gd_x)Be_{13}$  and  $[(U_{0.971}Th_{0.029})_{1-x}Gd_x]Be_{13}$ , compared to the multiple pair breaking theory for  $H_J = 0$  (solid lines) and  $H_J \neq 0$  (dashed lines).

of superconductivity, possibly involving ABM (Anderson-Brinkman-Morel) type triplet-spin pairing of superconducting electrons. On the other hand, singlet-spin and BW type triplet-spin superconductivity in  $(U_{0.971}Th_{0.029})Be_{13}$  would also be insensitive to the Gd exchange field in the presence of sufficiently strong spin-orbit scattering, although unphysically large values of  $\lambda_{so}$  would be necessary ( $\lambda_{so} \geq 300$ , corresponding to a spin-orbit scattering mean free path  $l_{so} \leq 0.02 \text{ \AA}$ ).

#### HIGH $T_c$ COPPER OXIDE SUPERCONDUCTORS

Recently, we have been involved in a detailed study of the physical properties of the  $RBa_2Cu_3O_{7-\delta}$  compounds where R is rare earth element (except for Pm), in addition to  $YBa_2Cu_3O_{7-\delta}$ . We found that all of the compounds exhibit superconductivity, except for  $R = Ce, Pr$  and  $Tb$ .<sup>14, 22, 23</sup> Shown in Figs. 3(a) and (b) are electrical resistivity  $\rho$ ,

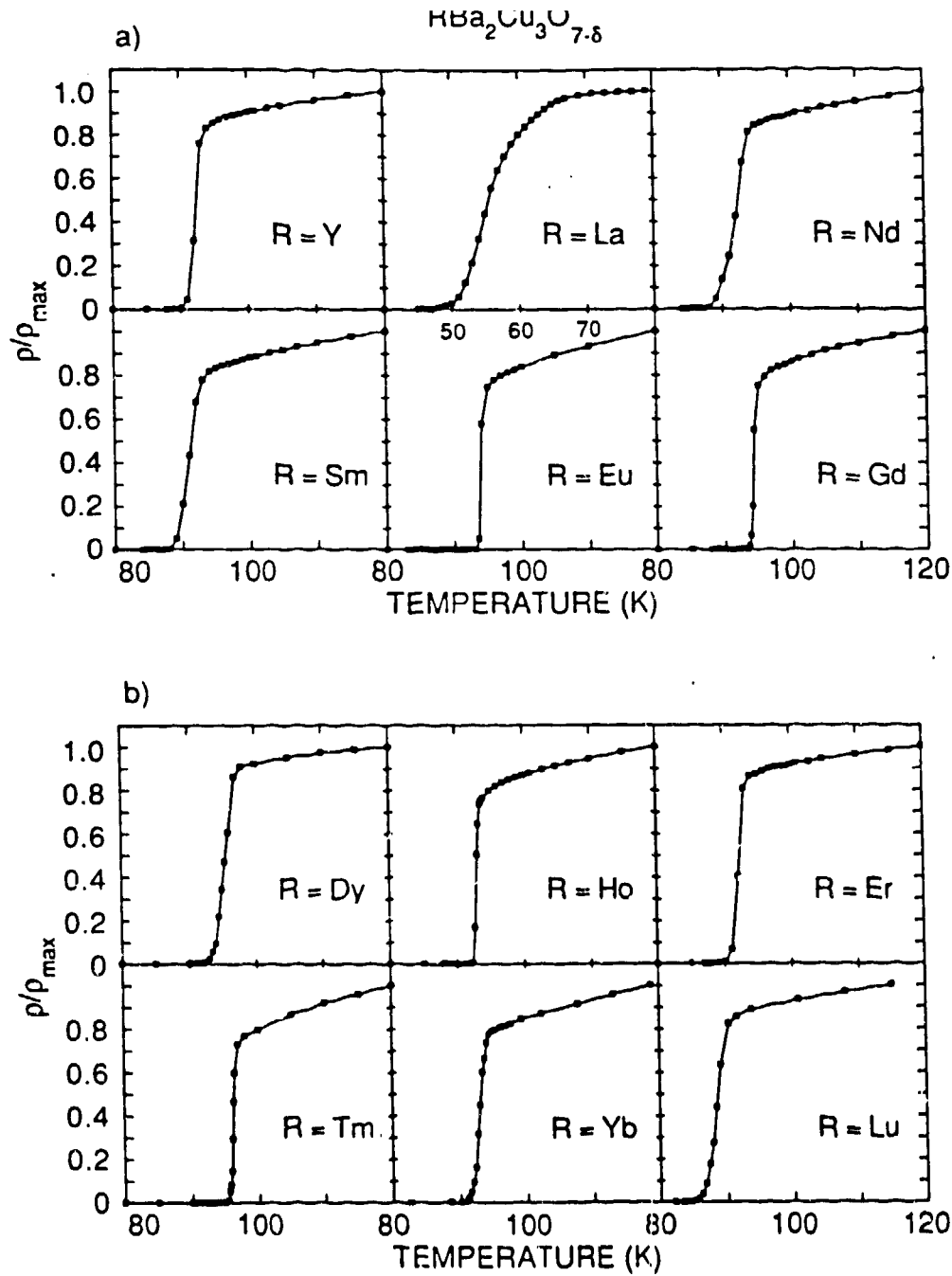


Fig. 3. Electrical resistivity  $\rho$ , normalized to its value at 120 K (80 K for La) for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with (a)  $R = \text{Y, La, Nd, Sm, Eu and Gd}$ , and (b)  $R = \text{Dy, Ho, Er, Tm, Yb and Lu}$ .

normalized to its value at 120 K (80 K for  $R = \text{La}$ ), vs temperature data for the superconducting  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds. The ratio of the room temperature value of  $\rho$  to the value of  $\rho$  right above  $T_c$  ranges from  $\sim 1.3$  for  $R = \text{Dy}$  to  $\sim 3.3$  for  $R = \text{Yb}$ , and it increases when the sample quality is improved. The superconducting transition temperature  $T_c$ , defined by the temperature at which  $\rho$  drops to 50% of its extrapolated normal state value, is typically between 90 K and 94 K, while the transition width  $\Delta T_c$ , defined by the temperatures at which  $\rho$  drops to 10% and 90% of its extrapolated normal state value, is between 2 K and 5 K, except for  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for which  $T_c \approx 60$  K and  $\Delta T_c \approx 11$  K. In general, the



more metallic samples, as indicated by a larger resistivity ratio, have narrower transition widths. The particularly low  $T_C$  for  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is consistent with other data,<sup>24</sup> although there is at least one report of a  $T_C$  onset of  $\sim 90$  K for this compound.<sup>25</sup>

Plots of the inverse susceptibility  $\chi^{-1}$  vs temperature are presented in Fig. 4 for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Ce}, \text{Pr}, \text{Nd}$  and  $\text{Sm}$  and in Fig. 5 for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$  and  $\text{Yb}$ . The lines in Figs. 4 and 5 represent fits of the  $\chi(T)$  data with the sum of a constant Pauli-like contribution and a Curie-Weiss term, i.e.,

$$\chi(T) = \chi_0 + N\mu_{\text{eff}}^2 / 3k_B(T - \theta) \quad (1)$$

where  $N$  is the Avogadro's number,  $\mu_{\text{eff}}$  is the effective moment, and  $\theta$  is the Curie-Weiss temperature. Values of  $\chi_0$ ,  $\mu_{\text{eff}}$  and  $\theta$  obtained from fits of Eq. (1) to the  $\chi(T)$  data are listed in Table 1. The experimental values of  $\mu_{\text{eff}}$  are in reasonable agreement with the theoretical  $R^{3+}$  free ion Hund's rule values of  $\mu_{\text{eff}}$ , which are also given in Table 1. The weakly temperature dependent Van Vleck susceptibility of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (not shown in Figs. 4 or 5) reveals that Eu is trivalent in this compound with a  $J=0$  ground state. The magnetic susceptibility of the  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds of the ions  $R = \text{Y}, \text{La}$  and  $\text{Lu}$  with empty or filled 4f electron shells can also be fitted by Eq. (1), yielding the values of  $\chi_0$ ,  $\mu_{\text{eff}}$ , and  $\theta$  given in Table 1, although it is not clear whether the Curie-Weiss contribution is due to magnetic impurities or is actually an intrinsic behavior of the compounds.

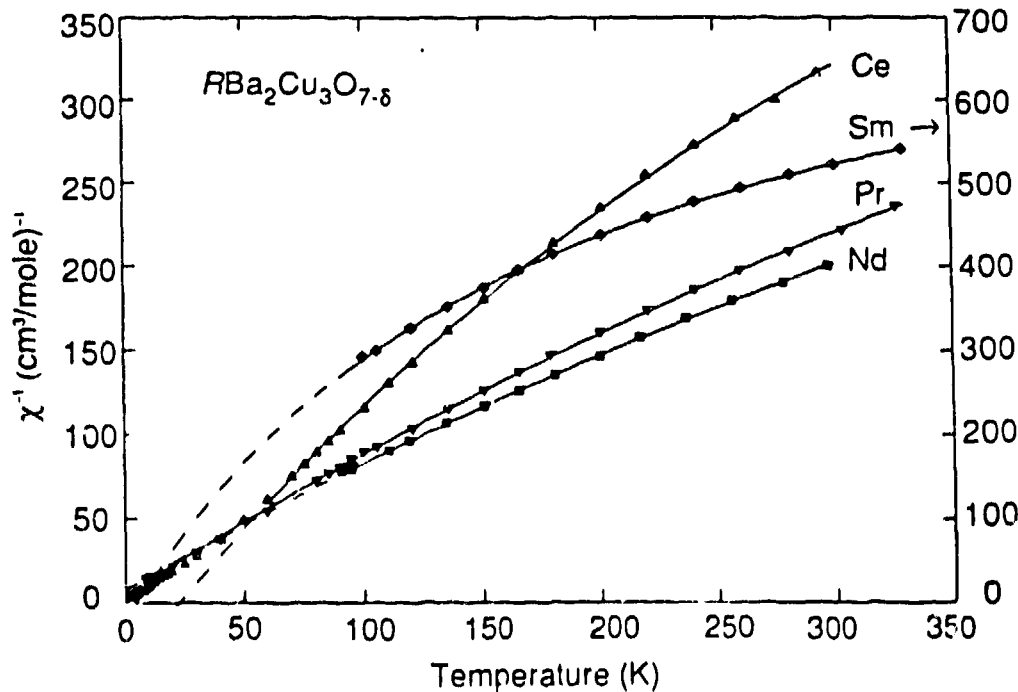


Fig. 4. Inverse magnetic susceptibility  $\chi^{-1}$  vs temperature for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Ce}, \text{Pr}, \text{Nd}$  and  $\text{Sm}$ .

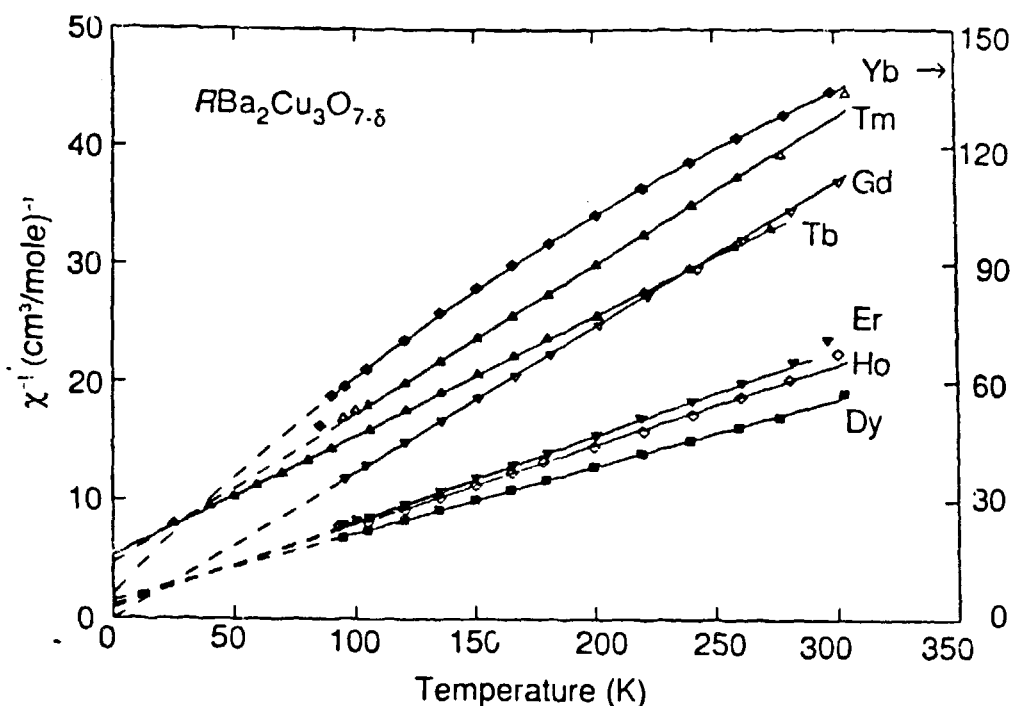


Fig. 5. Inverse magnetic susceptibility  $\chi^{-1}$  vs temperature for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Gd, Tb, Dy, Ho, Er, Tm}$  and  $\text{Yb}$ .

Table 1. Magnetic Susceptibility of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  Compounds  
 $\chi = \chi_0 + C/(T - \theta)$ ;  $C = N\mu_{\text{eff}}^2 / 3k_B$ .

R	$\chi_0 (\text{cm}^3/\text{mole}) \times 10^{-4}$	$\mu_{\text{eff}}^{\text{ex}} (\mu_B)$	$\mu_{\text{eff}}^{\text{th}} (\mu_B)$	$\theta (\text{K})$
Y	3.408	0.545	-	4.41
La	0.988	1.48	-	25.4
Ce	10.03	2.16	2.54	22.6
Pr	0.986	2.94	3.58	-5.25
Nd	1.08	3.10	3.62	-9.64
Sm	1.18	1.32	0.84	4.98
Gd*	-	8.05	7.94	0
Tb*	-	8.89	9.72	-52.4
Dy*	-	11.87	10.63	-27
Ho*	-	10.88	10.60	-17
Er*	-	10.48	9.59	-12
Tm*	-	7.96	7.57	-37
Yb	25.6	3.48	4.54	-9.49
Lu	-	2.11	-	18.5

\*Only the Curie-Weiss term  $C/(T-\theta)$  was used to fit Eq. (1) to the data.

Shown in Fig. 6 are specific heat  $C$  divided by  $T$  vs  $T$  data<sup>22</sup> for the related compound  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$  in the range  $0.5 \text{ K} < T < 60 \text{ K}$ . Low field magnetization measurements revealed a superconducting transition with an onset at 38 K for this sample.<sup>22</sup> However, since  $C(T)$  is dominated by the lattice contribution near  $T_c$ , it was not possible to extract the change in the electronic specific heat due to the superconducting transition from the data of Fig. 6, although the data do show a gradual change of slope over  $\sim 3 \text{ K}$  near 35 K. The  $C/T$  data below  $T_c$  ( $30 \text{ K} < T < 35 \text{ K}$ ) and above  $T_c$  ( $35 \text{ K} < T < 42 \text{ K}$ ) were then linearly extrapolated to 35 K, respectively, and yielded a difference  $\Delta C/T_c \cong 17 \text{ mJ/mole-K}^2$ . This value is comparable to the values obtained from other specific heat measurements on superconducting  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4-\delta}$  compounds.<sup>26-28</sup> The lattice contribution  $C_l = \beta T^3$  can be estimated from the low temperature  $C(T)$  data where the exponentially activated superconducting contribution becomes negligibly small. Shown in the inset of Fig. 6 is a plot of  $C/T$  vs  $T^2$  at low temperatures which can be described by the equation

$$C/T = \gamma + \beta T^2 \quad (2)$$

in the temperature range  $1.5 \text{ K} \leq T \leq 9 \text{ K}$  with values for  $\gamma$  and  $\beta$  of  $3.35 \text{ mJ/mole-K}^2$  and  $0.256 \text{ mJ/mole-K}^4$ , respectively. We do not know whether the non-zero  $\gamma$  is associated with part of the sample that remains normal down to the lowest temperatures, or whether it is an intrinsic feature of these extraordinary superconductors, e.g., due to vanishing of the superconducting energy gap over part of the Fermi surface. The Debye temperature  $\theta_D$  calculated from  $\theta$  equals 376 K. Another interesting feature is the deviation of the specific heat from the  $\beta T^3$  Debye behavior for  $T > 10 \text{ K}$ .

Shown in Fig. 7 are  $C/T$  vs  $T^2$  data for the 90 K superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for  $T < 60 \text{ K}$ . The  $C/T$  vs  $T^2$  data at low temperatures

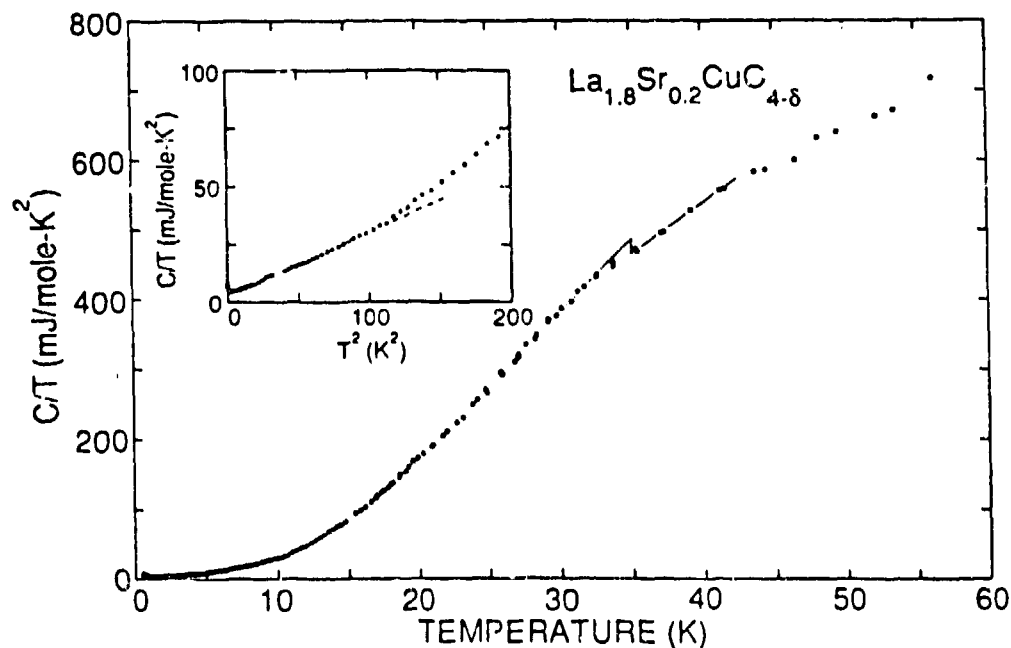


Fig. 6. Specific heat  $C$  divided by temperature  $T$  vs temperature for  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$ . Inset:  $C/T$  vs  $T^2$  below 14 K.

plotted in the lower inset of Fig. 7 can be described by Eq. (2) in the interval  $6 \text{ K} \leq T \leq 12 \text{ K}$  with the parameter values  $\gamma = 8.21 \text{ mJ/mole-K}^2$  and  $\beta = 0.449 \text{ mJ/mole-K}^4$ . The value of  $\beta$  corresponds to a Debye temperature  $\theta_D$  of 383 K, which is very close to  $\theta_D$  for  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$ . An upturn in  $C/T$  for  $T \leq 6 \text{ K}$  can be seen in the inset which may be associated with magnetic impurity phases in the sample. A plot in the upper inset of Fig. 7 of the difference  $\Delta C$  between the  $C(T)$  data and the calculated  $C(T)$  according to Eq. (2) vs  $T$  reveals a small peak in  $\Delta C(T)$  at  $T \approx 2 \text{ K}$  which is characteristic of magnetic order. Two features of the specific heat of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are similar to those observed in the specific heat of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_{4-\delta}$ , the non-zero  $\gamma$  in the superconducting state and the deviation of  $C(T)$  from the  $\beta T^3$  Debye behavior for  $T > 12 \text{ K}$ .

Shown in Fig. 8 are  $C(T)$  data for  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\text{TmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and, for comparison,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The peak in  $C(T)$  for the Ho compound at  $T \approx 5 \text{ K}$  appears to be an electronic Schottky anomaly associated with the crystalline electric field splitting of the  $\text{Ho}^{3+}$   $J=8$  Hund's rule groundstate. There is no trace of a Ho nuclear Schottky anomaly in the  $C(T)$  data, which is often observed for Ho compounds, indicating that the electronic ground state of Ho is probably a nonmagnetic singlet. The  $C(T)$  data for  $\text{TmBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have no distinguishable peaks at low temperature, although the specific heat is several times larger than that of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in this temperature region. The ground state of Tm in the crystalline electric field is probably a nonmagnetic singlet in this compound.

Upper critical field measurements in magnetic fields  $H$  of up to 9 tesla have been carried out on  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds where  $R = \text{Y, Eu, Gd, Dy, Ho, Er, Tm, and Yb}$ . These data were obtained by measuring

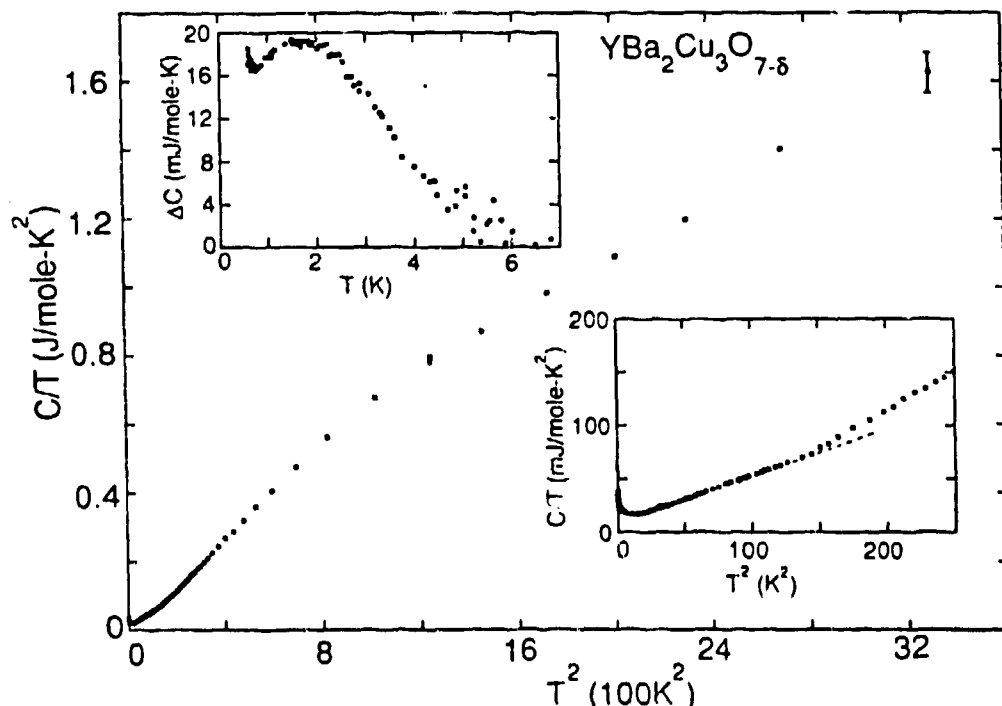


Fig. 7. Specific heat  $C$  divided by temperature  $T$  vs  $T^2$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Lower inset:  $C/T$  vs  $T^2$  below 16 K. Upper inset:  $\Delta C$  vs  $T$  below 7 K ( $\Delta C$  is defined in text).

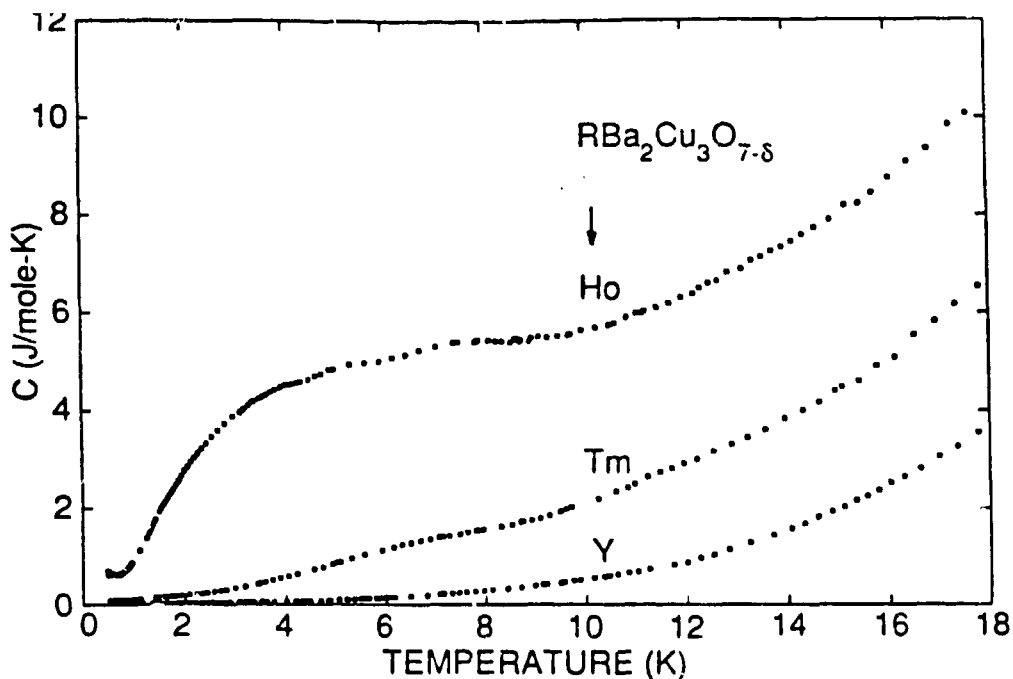


Fig. 8. Specific heat  $C$  vs temperature for  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Ho}$ ,  $\text{Tm}$  and  $\text{Y}$ .

the effect of  $H$  on the resistive transition between the normal and superconducting states. In Fig. 9 curves of  $\rho$  vs temperature for various applied fields are displayed for  $R = \text{Tm}$  and  $\text{Y}$ .<sup>29</sup> From these resistivity curves we extract the temperatures at which the resistivity drops to 0.5 of the extrapolated normal state resistivity for  $T \leq 100$  K; these temperatures vs the respective magnetic fields are plotted in Fig. 10 (square symbols). If we use the slope of a straight line drawn through these data and make extrapolations based on the standard, three dimensional, type II, dirty-limit Werthamer, Helfand, Hohenberg, and Maki (VHHM)<sup>20</sup> theory we obtain the remaining portion of the curves illustrated in Fig. 10.<sup>29</sup> Curves for minimum ( $\lambda_{so} = \infty$ ) and maximum ( $\lambda_{so} = 0$ ) paramagnetic limitation are shown, where  $\lambda_{so}$  is the spin-orbit coupling parameter. The extrapolations for  $R = \text{Tm}(\text{Y})$  provide  $H_{c2}(T = 0 \text{ K}) = 99\text{-}175$  tesla (60-71 tesla) with  $H_{c2}(T = 77 \text{ K}) \approx 36$  tesla (14 tesla). These extrapolations do not take into account the temperature variation of the normal-state electrical resistivity.<sup>29</sup> Included in this figure is the measured<sup>30</sup> upper critical field curve of  $\text{PbGd}_{0.2}\text{Mo}_6\text{S}_8$  with its present record of  $H_{c2}(T = 0 \text{ K}) \approx 60$  tesla. Figure 10 represents a rather dramatic view of the "new world of superconductivity" unfolded with the discovery of superconductivity in  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds.

The  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds with  $R = \text{Ce}$ ,  $\text{Pr}$  and  $\text{Tb}$  apparently fail to become superconducting because these  $R$  elements are not trivalent in this material. While  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  forms in a tetragonal phase closely related to the orthorhombic phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , the  $\text{Ce}$  and  $\text{Tb}$  counterparts form in a quite different crystal structure, which has not yet been identified. An attempt to substitute small amounts of  $\text{Ce}$ ,  $\text{Pr}$  and  $\text{Tb}$  for  $\text{Y}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  yielded multiphase samples for  $\text{Ce}$  and  $\text{Tb}$  substitutions, and single phase  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds for  $\text{Pr}$  substitutions. Measurements of  $\rho(T)$  in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0 \leq x \leq 0.6$ )

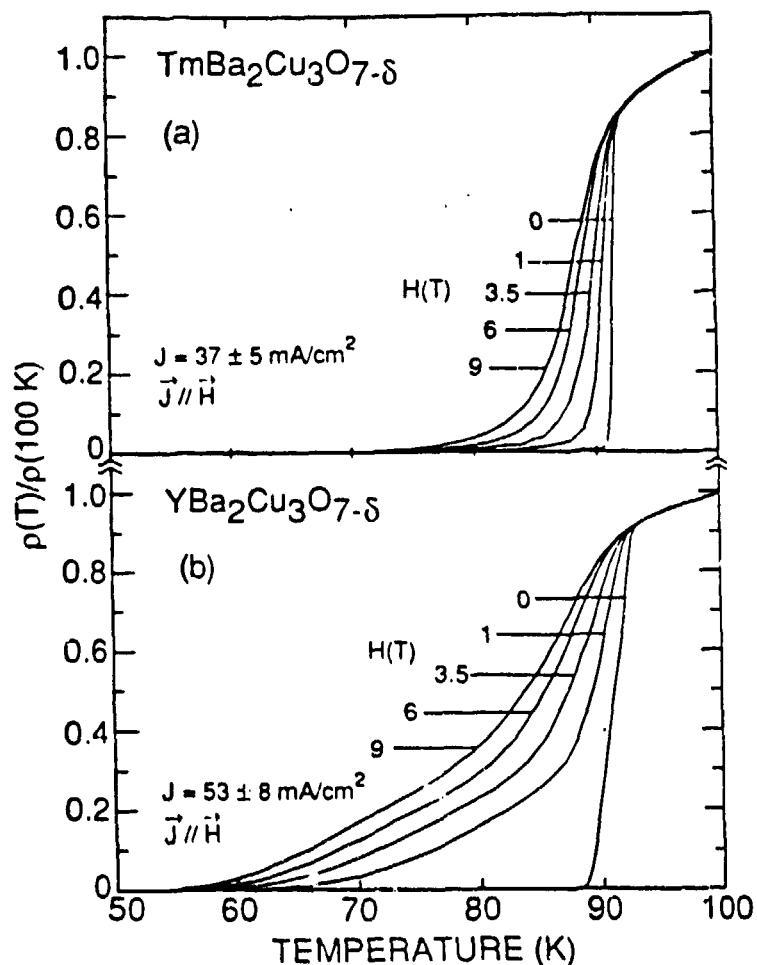


Fig. 9. Normalized resistivity  $\rho$  vs temperature for  $\text{TmBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in various applied magnetic fields between 0 and 9 T.

compounds (not shown) reveal a gradual transition from metallic to semi-conducting behavior as Pr is substituted for Y. The resistive superconducting transition curves broadened considerably upon substitution of Pr for Y, and  $T_c$  was depressed from 93 K at  $x=0$  to 34 K at  $x=0.5$ , as shown in Fig. 11, where the data points indicate transition midpoints and the vertical bars were taken between 10 and 90% of the resistive transition from the normal to the superconducting state.

Measurements of the electrical resistance under quasi-hydrostatic pressures to 150 kbar were performed on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and a plot of the normalized resistance  $R/R(120\text{ K})$  vs  $T$  at several pressures is shown in Fig. 12. The onset of the resistive transition from the normal to the superconducting state increases from  $\sim 95$  K at 8 kbar to  $\sim 106$  K at 149 kbar. This result suggests that yet higher values of  $T_c$  may be attainable in these oxides and related systems at ambient pressure.

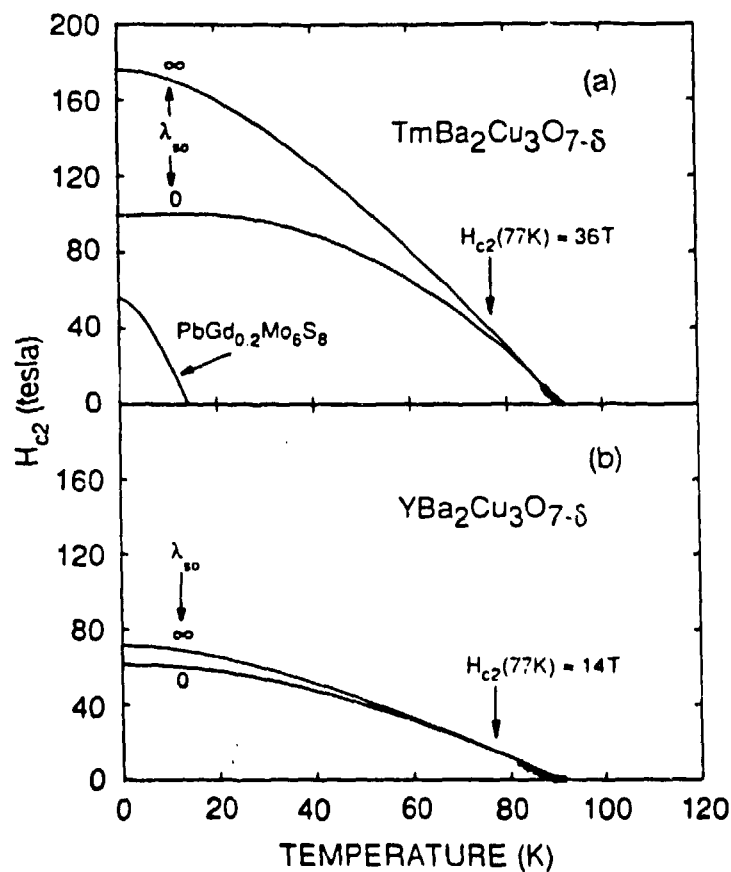


Fig. 10. Upper critical field  $H_{c2}$  (T) curves for  $\text{TmBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as extrapolated from the measured initial slope (heavy lines show extent of present measurements) in accord with standard WHHM theory.

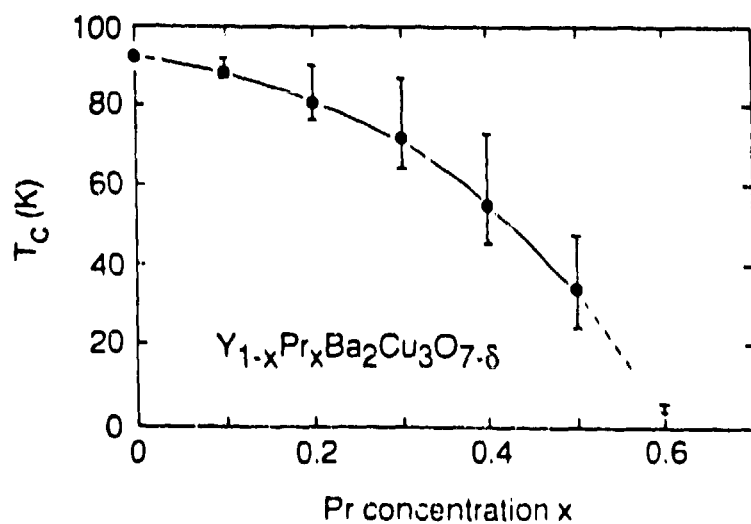


Fig. 11. Superconducting transition temperature  $T_c$  vs Pr concentration  $x$  for  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds. The line is a guide to the eye.

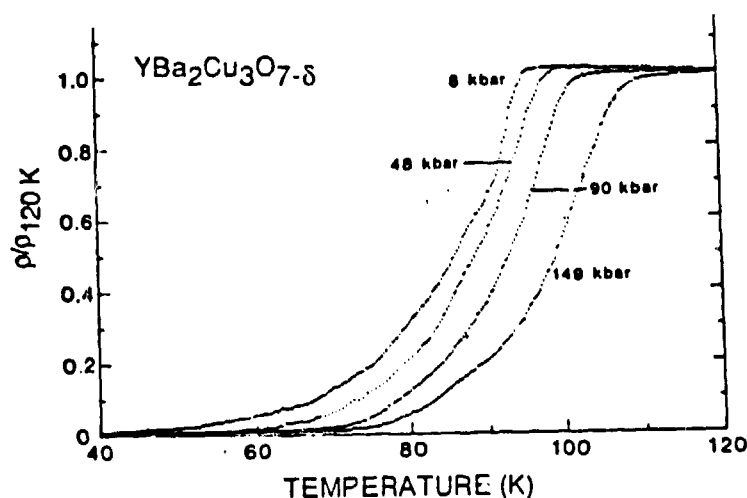


Fig. 12. Resistive superconducting transition curves for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at several pressures between 8 kbar and 149 kbar.

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